

Some observations on the structure of Durham polyacetylene

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The structure of polyacetylene produced from a precursor polymer is compared with that of polymer produced by a soluble Ziegler–Natta catalyst. X-ray diffraction shows that the precursor polyacetylene can be produced with a wide range of ordering from apparently amorphous to crystalline, although the ordering is never as high as that of polymer produced by the Ziegler–Natta route. An increase in ordering, as measured by X-ray peak width, has been observed during isomerization; this contrasts with normal polyacetylene where no change in order is found. Both forms of polyacetylene show a gradual shift in the interchain *d*-spacing from 395 pm (*cis/trans* mixed) to 365 pm (*trans*). Since only a single peak is found in this region the *cis*- and *trans*-forms are not phase-separated on a scale of 3 nm or more. Small-angle X-ray scattering also indicates that discrete crystalline and amorphous regions, as found in polyethylene, are not present

(Keywords: polyacetylene; precursor polymer; X-ray scattering; morphology; chain packing)

INTRODUCTION

Polyacetylene (PA) produced by the Shirakawa route, using a soluble Ziegler–Natta catalyst, crystallizes during polymerization to the *cis*-form. Subsequent heating converts this to the *trans*-form but the original morphology is preserved. Polyacetylene may also be prepared by the ‘Durham’ route¹ involving transformation of a soluble precursor polymer as shown in *Figure 1*. This PA has variously been described as amorphous¹ and crystalline² but certainly it is normally less ordered than Shirakawa polymer. Preparation of an oriented, highly crystalline form of Durham PA has been described^{3,4} and an X-ray study of the structure of this material is in an accompanying paper⁴.

In the absence of good, highly oriented fibres it has been difficult to determine unambiguously the crystal structures of PA. The *cis*-form has been reported to be orthorhombic with unit cell dimensions of 761, 447, 439 pm. The *trans*-form is monoclinic or orthorhombic. *Table 1* summarizes the unit cells that have been proposed for PA. The *trans*-conformation is extended 12% along the chain when compared to *cis*- but is contracted perpendicular to the chain by about the same amount such that the *cis*-form has a density close to that of the *trans*-isomer. The uncertainty over the crystal structure leads to an uncertainty in the density for *trans*-PA. A similar orthorhombic structure to *trans*-PA is observed for polyethylene (742, 495, 254 pm). It is close to a hexagonal packing of the chains such that it can be viewed as a slight deviation from close packing of smooth cylinders. Robin *et al.*⁵ find that the PA structure really only deviates from pseudo-hexagonal packing at greater than 80% conversion to the *trans*-isomer.

The isomerization occurs with a slow shift of the X-ray reflections, suggesting that it is an isomorphous change

with no loss of the crystal identity. Using the Scherrer formula with the width of the *hk0* reflections it is possible to estimate the extent of order from the X-ray coherence length perpendicular to the chain axis. This Robin *et al.*⁵ find to be 15 ± 3 nm and unchanged during isomerization. An equivalent measurement on polyethylene yields a ‘mosaic block’ size of 25–60 nm, which is much less than the actual extent of the crystals perpendicular to the chains⁶. After cold drawing the polyethylene mosaic size drops to about 10 nm.

During isomerization the reflections from the chain periodicity disappear, suggesting a loss of longitudinal coherence between neighbouring chains. These reappear when more than 80% of the polymer is in the *trans*-state at the same time as the packing becomes sufficiently regular to show splitting of the (110) and (200) reflections at 370 pm.

The ‘Durham’ polymer (*Figure 1*) has two bonds which should allow free rotation and two rigid bonds per repeat unit. Comparison of g.p.c. data⁷ with light scattering studies show that the precursor polymer, in solution in tetrahydrofuran, is more tightly coiled than polystyrene and that it has a chain expansion factor of about 6.8. This compares with a chain expansion of 6.3 in polyethylene measured as the radius of gyration of the random coil compared to that of an equivalent freely-jointed chain. Hence the precursor polymer is a randomly coiled, amorphous polymer. This Durham polymer can be converted to a predominantly *cis*-PA (typically 75% *cis*, 25% *trans*) by heating at 60°C for 45 min. At higher temperatures the material isomerizes to *trans*-PA. We have discussed the kinetics of transformation and isomerization processes elsewhere^{8,9}. Infra-red studies show that the isomerization is from 3 to 10 times faster than in Shirakawa polymer but with a similar activation

energy⁹. The higher rate is apparently due to the higher chain mobility in the less ordered Durham polymer and is in part due to the plasticizing effect of the fluoroxylene (1,2-bis(trifluoromethyl)benzene) released during the transformation. Raman spectroscopy indicates that the conjugation length of undisturbed *trans*-C=C sequences is shorter in Durham PA than in Shirakawa polymer¹⁰.

EXPERIMENTAL

The preparation of the precursor polymer has been described elsewhere¹. Precursor films were cast from a 5% solution in acetone in an argon atmosphere glove box (less than 10 ppm oxygen) on to PTFE. Nitrogen was bubbled through the solution prior to casting. The precursor films were transformed to PA at a range of temperatures (40°C–150°C) and times (10 min to 12 days), under vacuum (≈ 1 Pa). Typically the film thicknesses were 10 μ m. Pieces cut from the same films were used for infra-red measurements, density measurements and X-ray diffraction.

For X-ray diffraction the annealed films were transferred from the PTFE and held flat on an aluminium substrate with silicone grease around the edge of the film. The samples were examined in a vertical diffractometer in reflection mode with CuK α radiation. Samples were step scanned for 3 s over a limited 2θ range of 12–40°. The total time for data collection was about 1 h and repeat runs after 4 h exposure to air showed no changes. After 24 h in air the intensity of the PA peak is reduced by 50% and its width slightly increased (an increase in the doping peak at $2\theta = 12^\circ$ was not observed). Some thicker (30 μ m) films were prepared and were observed as double thicknesses out to $2\theta = 70^\circ$ to look for higher order reflections.

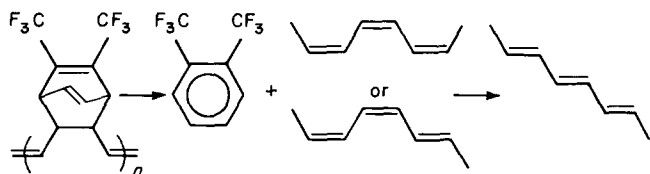


Figure 1 Durham route to polyacetylene

The small-angle scattering data were collected at SRS Daresbury using 4 layers of PA in a traditional pinhole camera with an X-ray wavelength of 160 pm and a position sensitive detector.

Density measurements were carried out by flotation in carbon tetrachloride–toluene mixtures.

RESULTS

A predominantly *cis* sample was prepared by slow transformation of the precursor polymer at 60°C. The X-ray data, Figures 2 and 3, show a main peak at $d = 395$ pm and a broad weak peak at $d = 230$ pm. This polymer may still contain some residual trapped fluoroxylene. The main peak corresponds to the (200, 110) peak seen by Robin *et al.*⁵ for *cis*-PA at 380 pm. The width of this peak can be interpreted to give an apparent coherence length, which can be compared with other polymers, using the Scherrer formula¹¹.

$$L = k \cdot \lambda / \beta_{1/2} \cdot \cos \theta$$

where L is the apparent coherence length and $\beta_{1/2}$ is the peak width at half height (in radians), corrected for instrumental broadening. In the present case the correction is negligible for these broad peaks. Taking $k = 1$ and $\beta_{1/2} = 4^\circ$ (2θ CuK α) we obtain $L = 2.2$ nm, much lower than for Shirakawa PA.

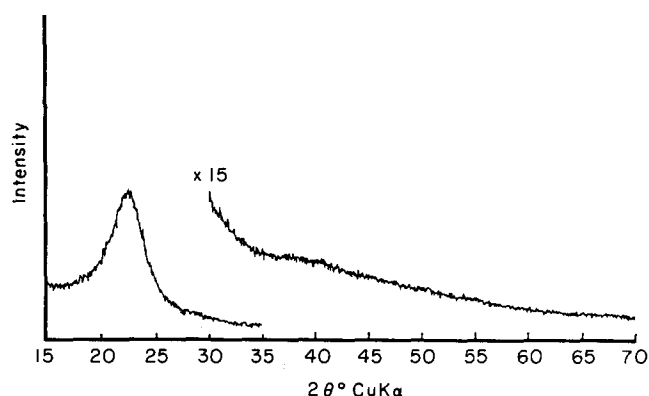


Figure 2 Wide-angle X-ray scattering from predominantly *cis* polyacetylene

Table 1 X-ray structures and densities of polyacetylene

Form	Structure	a (pm)	b (pm)	c ^a (pm)	d obs	Density (g cm ⁻³)		Ref.
						X-ray	Flotation	
<i>cis</i> ^b	orthorhombic	761	447	439	381	1.16		21
<i>cis</i>	orthorhombic	768	446	438	384	1.15		23
<i>cis</i>	orthorhombic	766	442	438	386	1.16		24
<i>cis</i> ^a					395			^a
<i>trans</i> ^b	monoclinic	746	408	246	356, 372	1.15		5
<i>trans</i>	monoclinic	732	424	246	365	1.13		13
<i>trans</i>	monoclinic	738	409	246	365	1.17		24
<i>trans</i> ^c	orthorhombic	726	424	246	365	1.13		4
<i>trans</i>							1.2	25
<i>trans</i>	annealed < 100°C						1.10	^a
<i>trans</i>	annealed 150°C						1.13	^a

^a Chain axis direction

^b Shirakawa polymer

^c Durham polymer

^d This work

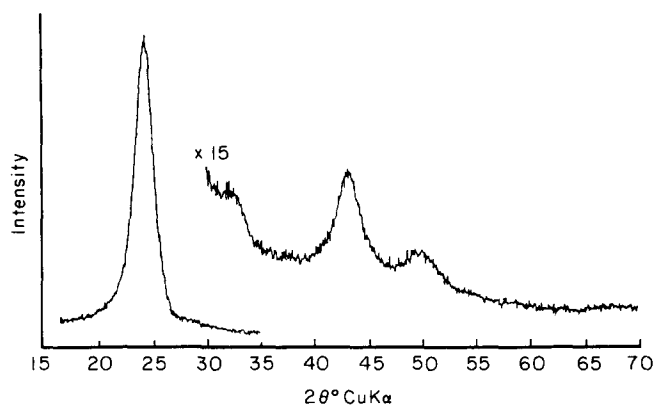


Figure 3 Wide-angle X-ray scattering from *trans* polyacetylene

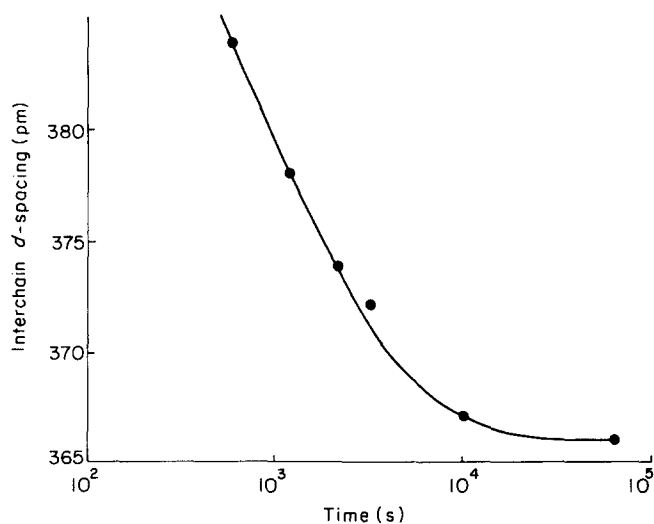


Figure 4 Variation in interchain *d*-spacing with time of annealing at 90°C

On heat treatment at 90°C the polymer isomerizes from *cis*- to *trans*-PA. The *d*-spacing of the diffraction peak decreases as shown in Figure 4 and reaches a limit of 365 pm; the peak width also decreases during isomerization. This corresponds to the broad double peak of *trans*-PA identified by Robin *et al.*⁵ as (200) 372 pm and (110) 356 pm. As shown in Figure 5 this shift in peak position correlates with the percentage of *cis* measured by i.r. spectroscopy. Measurements for other isomerization temperatures, also shown in Figure 5, show a similar trend and fit the same line. During isomerization the peak position moves gradually. There is no evidence for two separate peaks corresponding to discrete *cis*- and *trans*-regions. The peak width initially decreases during the isomerization process (Figure 6) and then levels out and starts to rise slowly at much longer times. Figure 7 shows the apparent coherence lengths for samples fully transformed at different transformation temperatures up to 150°C. The highest value, which is found after 150°C isomerization, is 7 nm. This represents a minimum value because the peak may be doubled. Figure 8 shows a sample well isomerized and annealed at 140°C where the main peak shows some sign of (110), (200) splitting indicating a departure from pseudo-hexagonal packing.

The density of each of twenty samples of Durham PA transformed below 100°C, with *cis* contents between 5% and 60%, was measured using a density gradient column. No change of density with *cis* content was observed, the density being $1.10 \pm 0.01 \text{ g cm}^{-3}$ for all samples. After

transformation at 150°C the density increased to $1.13 \pm 0.01 \text{ g cm}^{-3}$. The density of highly oriented drawn films was $1.15 \pm 0.01 \text{ g cm}^{-3}$.

DISCUSSION

Durham PA is produced by solid state reaction from an amorphous polymer. It is thus of interest to decide how much ordering occurs at the different stages during the conversion from the precursor and during the isomerization. In interpreting this it is valuable to consider analogies with ordering of other polymers but it is necessary to bear in mind that PA is a very stiff chain and therefore will respond differently in comparison with flexible polymers such as polyethylene.

A comparison of the X-ray diffraction data with those for *cis*- and *trans*-Shirakawa polymer⁵ shows that the Durham samples are less ordered. The interchain diffraction peak is significantly broader and the higher angle data substantially weaker than in the Shirakawa samples. A simple interpretation is that the Durham PA is amorphous. This seems to be unlikely, at least for the well-annealed *trans*-material, as several peaks are clearly observed. Apparent coherence lengths, calculated from X-ray peak widths, are compared in Table 2 for a number of amorphous and crystalline polymers and Durham PA. Whilst coherence length does depend upon morphology, the variations are not great for most polymers. The assignment to amorphous or crystalline in Table 2 depends on electron or optical microscopy. It can be seen that, although there are groups of polymers which are

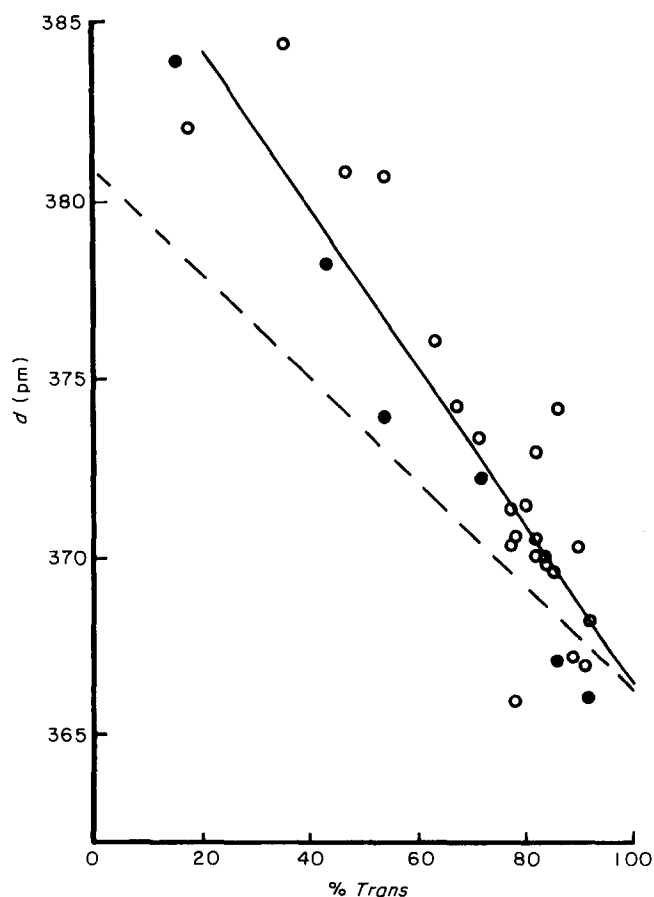


Figure 5 Correlation between X-ray *d*-spacing and content of *trans* isomer determined by infra-red spectroscopy. (—) Durham polymer, (---) relationship for Shirakawa polyacetylene¹³, (●) samples annealed at 90°C

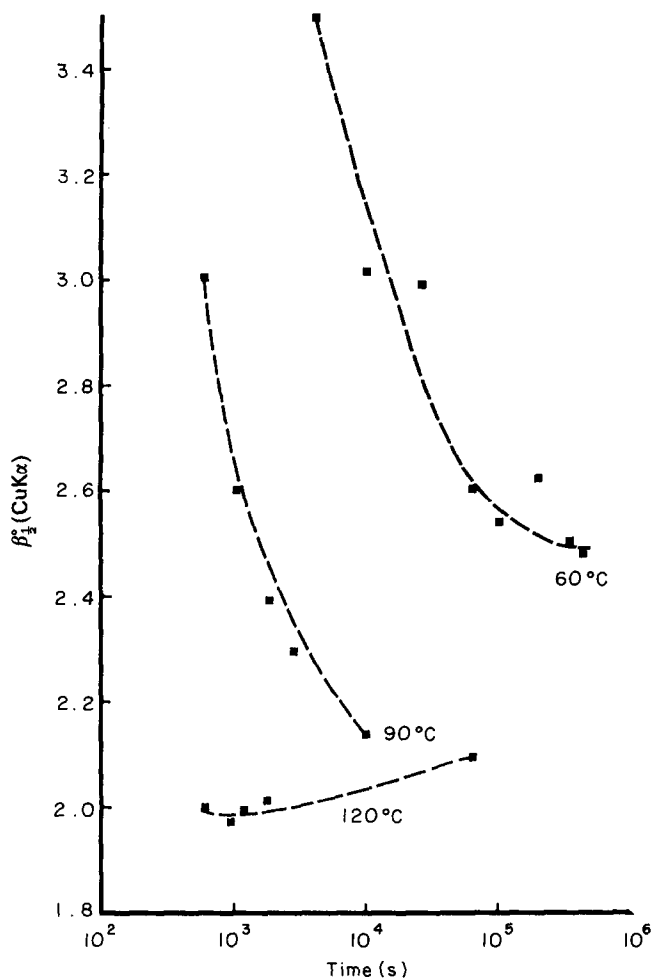


Figure 6 Change in X-ray peak width (full width at half maximum) with annealing time at 60°C, 90°C and 120°C

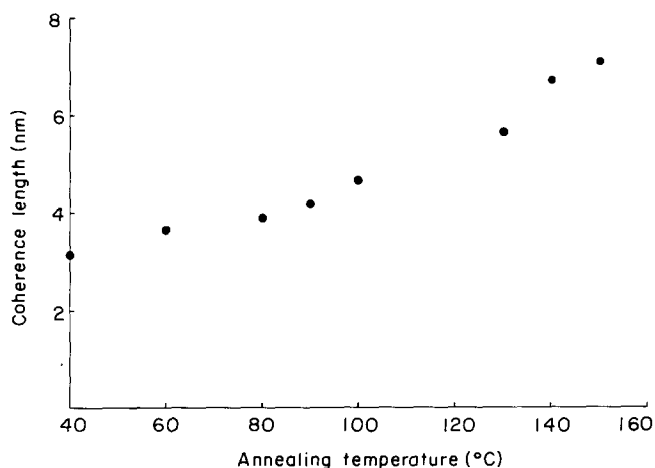


Figure 7 Variation of coherence length, determined from X-ray peak width, with temperature of transformation and annealing

clearly amorphous or crystalline, there is a number of materials which are intermediate on the basis of X-ray diffraction. The apparent coherence length of Durham PA varies over the range from typical amorphous polymers to accepted crystalline materials. In Table 3 the densities of amorphous and crystalline forms of several polymers are compared. It can be seen that the density of Durham PA is intermediate between those typical of a crystalline and of an amorphous polymer until annealed at 150°C.

The final *trans*-state after annealing at high temperatures appears to be crystalline, although still not to the same extent as Shirakawa polymer. The density is only slightly below that calculated for the crystalline phase. The diffraction data (Figure 3) are consistent with published orthorhombic (or monoclinic) structures (see e.g. ref. 13), whilst the main peak in Figure 7 shows some sign of splitting, indicative of a small departure from pseudo-hexagonal packing (as observed by Pouget *et al.*¹⁵).

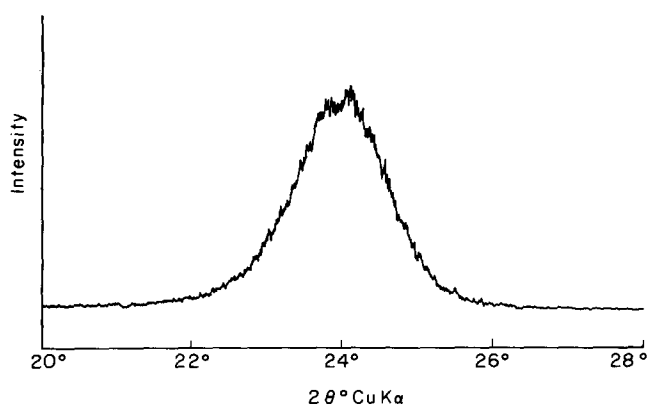


Figure 8 X-ray diffraction from a sample transformed at 140°C showing a narrow and split peak

Table 2 X-ray coherence lengths for typical polymers^a

Polymer	Coherence length (nm)	Accepted structure
Polyacrylamide	0.6	Amorphous
Poly(methyl methacrylate)	1.4	Amorphous
<i>cis</i> -1,4-Polybutadiene	1.5	Amorphous
Polyisobutylene	2.0	Amorphous
Polystyrene (atactic)	1.6	Amorphous
Poly(vinyl alcohol)	4.1	Crystalline
<i>cis</i> -Polyisoprene	6.0	Amorphous
Poly(ethylene terephthalate)	6.5	Amorphous
Polyacrylonitrile	8.9	Amorphous
Polystyrene (isotactic)	8.9	Crystalline
<i>trans</i> -1,4-Polybutadiene	18.0	Crystalline
High density polyethylene	18.0	Crystalline
Linear polyethylene	30.0	Crystalline
Poly(methylene oxide)	30.0	Crystalline
Shirakawa PA	15 (ref. 5)	Crystalline
Durham PA (<i>cis-trans</i>)	2.6	—
Durham PA (<i>trans</i> , 60°C)	3.6	—
Durham PA (<i>trans</i> , 150°C)	7.1	—

^aCalculated from data in ref. 6

Table 3 Amorphous and crystalline densities of polymers^a

Polymer	Crystalline density (g cm ⁻³)	Amorphous density/crystalline density
Polyethylene	1.00	0.86
Nylon-6,6	1.24	0.88
Polypropylene	0.94	0.90
<i>trans</i> -1,4-Polybutadiene	1.04	0.87
<i>cis</i> -1,4-Polybutadiene	1.01	0.91
Poly(ethylene terephthalate)	1.47	0.91
Polystyrene	1.13	0.93
Poly(vinyl alcohol)	1.35	0.94
Durham PA (<i>trans</i> , 60°C)	1.15	0.96
Durham PA (<i>trans</i> , 150°C)	1.15	0.98

^aCalculated from data in ref. 6

The diffraction pattern in Figure 3 can be analysed for the paracrystalline contribution to disorder as has been done for oriented material by Sokolowski⁴, who assumes that the broadening due to any peak doubling is small. Wunderlich⁶ has discussed the application of this method to unoriented polymers. The trend of peak widths with increasing scattering angle for this high transformation temperature sample is very similar to that found for the oriented material⁴, i.e. both show some paracrystalline disorder. Again the major contribution to the width of the main peak comes from the small crystallite size.

It is less clear how the state of the *trans*-material formed at low temperatures should be described. One analogy is with polyethylene which is a two phase material containing 20–70% amorphous polymer with a density 85% of that of the crystals. The crystals are lamellae a few tens of nm thick parallel to the chain axis by several μm wide. In PA the density difference between the amorphous and crystalline phases is 3–5%, while in PE it is 15%. Nevertheless if PA were a two-phase structure we would expect to see a small-angle X-ray scattering peak due to the amorphous-crystal alternation. We see no such peak, as is shown in Figure 9, where we compare scattering from Durham PA with that from a sample of low density polyethylene. The LDPE sample was quenched and annealed for 24 h at 60°C; it had a typical two-phase structure with lamellae about 17 nm thick.

A polymer which may be a better analogy for PA is polytetrafluoroethylene¹². Below 20°C this stiff chain polymer crystallizes with a triclinic structure with the chains as slowly twisting helices with each unit being twisted about 15 degrees out of the *trans*-position. At 20°C there is a transition with a 1% expansion to a hexagonal structure with a slightly slower twist. At 30°C there is an 0.2% volume increase to a hexagonal structure with chains disordered along the axis. This disordered crystalline state would seem to be similar to that which Pouget finds in unannealed *trans*-PA and to the *trans*-state reported by Fincher *et al.*¹³. This is apparently metastable and slowly converts to the more ordered form. In polytetrafluoroethylene the crystalline order perpendicular to the chains remains extensive.

A third possible analogy is the smectic phase identified in quenched polypropylene^{14,15}. This is a highly disordered hexagonal phase which can transform to the normal monoclinic structure on annealing.

We believe that the original amorphous precursor polymer converts to a swollen amorphous PA as the fluoroxylyene is released. As this solvent diffuses out of the film we observe an abrupt decrease in the diffusion coefficient when about 60% has left (Figure 10). During

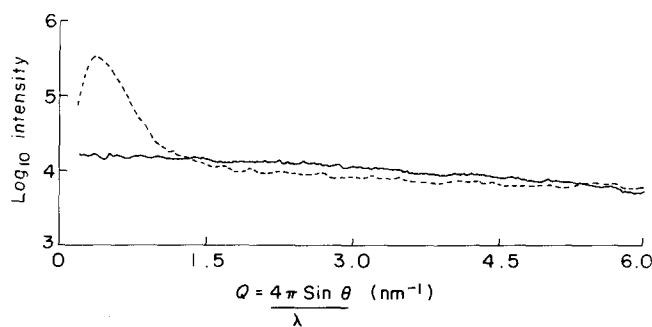


Figure 9 Small-angle X-ray scattering (—) from *trans* Durham polyacetylene as compared with polyethylene (---). Note the absence of a peak in scattered intensity in polyacetylene

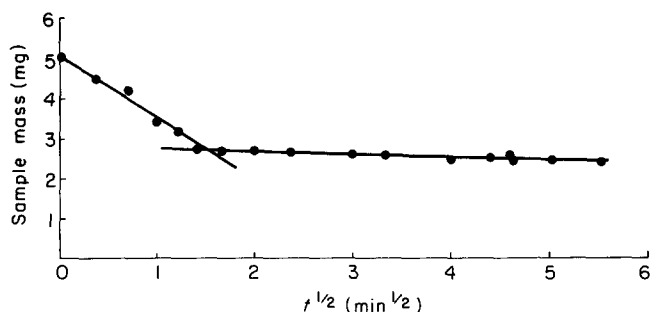


Figure 10 Weight loss at 50°C *in vacuo* of predominantly *cis* Durham polyacetylene due to diffusion out of released fluoroxylyene. Diffusion rate slows when about 50% of the fluoroxylyene has been lost

isomerization, the resulting *cis/trans* polymer shows an increase in order of this pseudo-hexagonal packing perpendicular to the chain axis. However this process is limited by the randomly coiled path of the chains which cannot be modified without extensive motion along the whole chain length. After prolonged annealing the crystal structure starts to convert into the orthorhombic form as the chains come into register and the twisted regions are excluded to the zones between the crystals. This is accompanied by an increase in density to 1.13 g cm^{-3} .

In conclusion the differences and similarities between Durham PA and Shirakawa PA are summarized. The continuous shift in interchain *d*-spacing during isomerization (Figure 5) is similar to that observed by Riekel¹⁶ and Robin *et al.*^{5,17}. The final *trans* *d*-spacing of Durham PA is very close to that reported for Shirakawa PA^{13,17–19}. However, the inter-chain spacing of the predominantly *cis*- Durham PA tends to be greater^{17,20–22} probably because it is amorphous. Durham PA increases in order on annealing while Shirakawa polymer does not^{5,16,17}. The degree of order depends on the isomerization temperature.

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